Phonon drag effect in single-walled carbon nanotubes

V. W. Scarola and G. D. Mahan
Department of Physics, 104 Davey Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802
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A variational solution of the coupled electron-phonon Boltzmann equations is used to calculate the phonon drag contribution to the thermopower in a one-dimensional system. A simple formula is derived for the temperature dependence of the phonon drag in metallic single-walled carbon nanotubes. Scattering between different electronic bands yields nonzero values for the phonon drag as the Fermi level varies.

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I. INTRODUCTION

Since their discovery,[1] carbon nanotubes have provided a testbed for fundamental and applied physics. Characterization of these new systems is crucial for future progress. The thermopower of a material is an intrinsic quantity which yields important information related to the electronic band structure, electron-phonon coupling parameters, and relaxation rates of the system. Recent experiments on mats of single walled carbon nanotubes[2–8] have found surprisingly large values for the thermoelectric power ($\sim 50\ \mu$V/K) under various ambient conditions. When the thermopower is plotted versus temperature most of the data show a quasilinear behavior at temperatures greater than 200 K. Thermopower linear in temperature suggests that conduction through metallic tubes dominates the thermopower at these temperatures. However, some data show nonlinearities below ~ 200 K. Here a peak in the thermopower is observed. The origin of this peak is the subject of much debate. Several effects that could lead to such behavior have been discussed in the literature. These include parallel transport through semiconducting tubes,[2] a one-dimensional Kondo effect,[4] and the phonon drag effect. Semiconducting tubes are not expected to contribute much to the thermopower because metallic tubes have a larger electrical conductivity.[3] The Kondo effect has been invoked to explain the large peak in samples containing magnetic impurities. However, a smaller, broad peak remains when the magnetic impurities are removed and therefore does not explain the universality of the low temperature nonlinearity in samples without magnetic impurities.

Turning to the phonon drag effect, very little theoretical work has been done to calculate the phonon drag contribution to the thermopower in metallic carbon nanotubes. Rough low-temperature estimates often quote the result

$$S_{\text{drag}} \propto C_v , \tag{1}$$

where C_v is the lattice specific heat. However, this formula assumes that phonons scatter electrons within one parabolic band and that electron-phonon scattering acts as the dominant phonon decay mechanism. Applying Eq. (1) to nanotubes with two bands, particle and hole, yields a negligible contribution to the thermopower due to drag because the particle and hole contributions cancel.

The objective of this work is to extract the temperature dependence of the phonon drag contribution to the thermopower for a one-dimensional (1D) system, within the linear band approximation. We consider a model wherein mechanisms other than electron-phonon scattering limit phonon lifetimes. We derive an expression for the phonon drag in these systems using a solution of the coupled electron-phonon Boltzmann equations. We find that *inter*band scattering gives a non-zero contribution to the thermopower when the Fermi level does *not* lie at the band crossing. Interband transitions near the Fermi level contribute appreciably to the phonon drag thermopower. Our results can be summarized in the following formula.

$$S_{\text{total}} = AT + \frac{B}{T^{m+1}} \frac{\text{sgn}(-\mu)}{e^{2c|\mu|/v k_B T} - 1} \left(1 + \frac{c|\mu|}{v k_B T} \right) \tag{2}$$

in the limit

$$k_B T \ll |\mu| \ll \frac{k_B T_D v}{2c},$$

where A and B are fitting parameters, μ is the energy difference between the Fermi level and the band crossing, v the electron speed, c a typical phonon speed, and T_D the Debye temperature. m parametrizes the temperature dependence of the phonon relaxation time. In metals one typically finds $m \sim 1$ at temperatures near the Debye temperature. The term linear in temperature is the usual diffusive contribution for metals and the second term is our result for the phonon drag part at low temperatures. This formula yields a peak, due to phonon drag. We therefore associate the phonon drag effect with the low temperature nonlinearities observed in thermopower measurements on single-walled carbon nanotubes.

The plan of the paper is as follows. In Sec. II we outline the basic theory of thermopower measurements in metals. In Sec. III Bailyn's theory of phonon drag in metals is reviewed. In Sec. IV we apply Bailyn's theory to a simple 1D model of single walled, (10,10) armchair carbon nanotubes. Here we derive an expression for the phonon drag in these systems. In Sec. V we extract a simple formula by making a low temperature approximation. In Sec. VI we conclude by discussing the limits of our approximations.

II. THERMOPOWER DUE TO ELECTRON DIFFUSION AND PHONON DRAG

The application of a temperature gradient to a metal leads to the diffusion of charge carriers from the warm to the cold

end of the sample. The thermopower measures the charge build up across the sample. It is given by $S = \lim_{\Delta T \to 0} \Delta V / \Delta T$, where ΔV and ΔT are the potential and temperature differences across the sample, respectively. The thermopower due to diffusion S_{diff} can be calculated from the standard set of transport coefficients. The transport coefficients can in turn be derived from the Boltzmann equation for the electron distribution function. A general argument leads to the Mott expression for the thermopower due to diffusion

$$S_{\text{diff}} = \frac{-\pi^2}{3} \frac{k_B^2 T}{|e|} \left(\frac{\partial \ln \sigma}{\partial E} \right)_{EF}, \tag{3}$$

where E is the energy, σ the electrical conductivity, and EF the Fermi energy. When there is more than one band present the thermopower due to each band adds

$$S_{\text{diff}} = \frac{\sum_l \sigma_l S_{\text{diff}}^l}{\sum_l \sigma_l}, \tag{4}$$

where l is the band index.

We apply the above equations to the case of metallic carbon nanotubes by considering electrons in one dimension. The electronic states fill two overlapping, parabolic bands, the particle and hole bands, up to the Fermi level. With only one parabolic band we expect the diffusive part of the thermopower in a metal to vary linearly with temperature. The factor $(\partial \ln \sigma / \partial E)_{EF}$ depends on the details of the system, including the density of states. However, with two bands present, the thermopower due to states filling the hole band cancels the contribution from the particle band when the Fermi level lies at the band crossing. Within this approximation we have no net contribution to the thermopower in a metallic tube.

When the Fermi level is allowed to move within the rigid π bands the resulting thermopower is nonzero.[3] Recent calculations show that an enhancement in the density of states due to impurities[3,9,10] or tube-tube interactions[2,11,12] may generate large contributions to the thermopower through the term $(\partial \ln \sigma / \partial E)_{EF}$. We therefore consider the following standard form for the diffusive contribution to the thermopower in metals:

$$S_{\text{diff}} = AT, \tag{5}$$

where the constant A is a fitting parameter which may vary with the Fermi level. Recent experiments on mats of single walled, carbon nanotube bundles do indeed show this behavior at large temperatures ($T > 200$ K).[3,13]

An anomalous peak in the thermopower appears at low temperatures in several different experiments on single-walled and multiwalled carbon nanotubes. In standard thermopower measurements of 3D metals such behavior is often associated with the phonon drag effect whereby the phonon flux from the hot end of the sample to the cold end drags additional charge carriers to the cold end of the sample via momentum transfer. This effect adds to the thermopower in conventional metals

$$S_{\text{total}} = S_{\text{diff}} + S_{\text{drag}}. \tag{6}$$

Standard, low temperature estimates of the phonon drag contribution to the thermopower rely on the relation

$$S_{\text{drag}} \simeq \frac{-C_v t}{3n|e|}, \tag{7}$$

where C_v is the lattice specific heat, n the carrier density, and the t is the transfer factor. t is a rough estimate of the probability that a phonon collides with an electron relative to all scattering events. In one dimension the lattice specific heat is nearly linear in temperature[14,15] and does not provide the nonlinear temperature dependence required to explain the peak observed in measurements on carbon nanotubes.[16] Moreover, if we consider only intraband scattering, the contributions from states filling the electron and hole bands should cancel to give no net drag.

The above formula for the drag contribution cannot be applied to metallic carbon nanotubes for two reasons. The derivation of the above formula[18] relies on a free, electronic band structure where transitions lie only within the parabolic bands. It also assumes that the dominant decay mechanism for phonons is electron-phonon scattering. Below we derive a new formula for the low temperature phonon drag contribution to the thermopower in one dimension. We find a nonzero contribution to the phonon drag part of the thermopower when we include transitions between two linear bands and assume that the dominant decay mechanism for phonons is *not* electron-phonon scattering.

III. BAILYN FORMALISM FOR PHONON DRAG

The phonon drag contribution to the thermopower in a metal may be calculated by solving the coupled electron-phonon Boltzmann equations. In this section we briefly review Bailyn's formalism for calculating the phonon drag. Following Ref. 19 we write the Boltzmann equation for the electron distribution function, f, in the relaxation time approximation. Using first order perturbation theory for the electron transition probabilities one finds

$$\begin{aligned} \left(\frac{\partial f}{\partial t} \right)_{\text{coll}} = \sum_{\vec{k}',l'} C_{\vec{k},\vec{k}'j} (\delta(-)\delta_{\vec{k}',\vec{k}+\vec{q}} \times \{ -N(\vec{q}j) f(1-f') \\ + [N(\vec{q}j)+1] f'(1-f) \} + \delta(+)\delta_{\vec{k}',\vec{k}+\vec{q}} \{ -[N(\vec{q}j) \\ + 1] f(1-f') + N(\vec{q}j) f'(1-f) \}) - (f-f_0)/\tau(\vec{k}), \end{aligned} \tag{8}$$

where $N(\vec{q}j)$ is the phonon distribution function, $\omega = c|q|$ is the frequency of a phonon with speed c, f_0 is the Fermi-Dirac distribution function, and $\tau(\vec{k})$ is the relaxation time due to the electron-electron interaction. We define the energy delta functions

$$\delta(\pm)\equiv\delta[E(\vec{k}'l')-E(\vec{k}l)\pm\hbar\omega]. \tag{9}$$

The factor $C_{\vec{k},\vec{k}'j}$ is related to the electron-phonon matrix elements

$$C_{\vec{k},\vec{k}'j}=\frac{\mathcal{M}(\vec{q}j)}{2\hbar\omega(\vec{q}j)}, \tag{10}$$

where $\mathcal{M}(\vec{q}j)\equiv|\langle\vec{k}'l'|\vec{\nabla}U\cdot\vec{\epsilon}(\vec{q}j)|\vec{k}l\rangle|^2/MN_c$ is the square of the matrix element for the scattering of an electron from wave vector $\vec{k}$ and band l to wave vector $\vec{k}'$ and band l' by a phonon of wave vector $\vec{q}$ and polarization j. Here $\vec{\nabla}U$ is the gradient of the ion potential, N_c the number of cells in the periodic block, M the ion mass, and $\vec{\epsilon}(\vec{q}j)$ the phonon polarization vector. The above matrix element ignores Umklapp scattering.[20]

From the above expression for the electron distribution function we can read off the necessary terms for the phonon Boltzmann equation. The second and third terms show gains in the phonon distribution. The first and fourth terms show losses in the phonon distribution function. This gives

$$\begin{aligned}-\left(\frac{\partial N(\vec{q}j)}{\partial t}\right)_{\text{drift}}=\left(\frac{\partial N(\vec{q}j)}{\partial t}\right)_{\text{coll}}&=\sum_{\vec{k},\vec{k}'}C_{\vec{k},\vec{k}'j}(\delta(-)\delta_{\vec{k}',\vec{k}+\vec{q}}\\&\times\{-N(\vec{q}j)f(1-f')+[N(\vec{q}j)+1]f'\\&\times(1-f)\}-\delta(+)\delta_{\vec{k}',\vec{k}+\vec{q}}\{-[N(\vec{q}j)\\&+1]f(1-f')+N(\vec{q}j)f'(1-f)\})\\&-[N(\vec{q}j)-N_0]/\tau(\vec{q}),\end{aligned} \tag{11}$$

where $\tau(\vec{q})$ is the phonon relaxation time and N_0 is the Bose distribution. The above two equations for the electron and phonon distribution functions can be solved using a variational procedure. From the relevant transport coefficients the phonon drag contribution to the thermopower can be extracted. The most general form for which was derived in Ref. 21.

$$\begin{aligned}S_{\text{drag}}=\frac{2|e|k_B}{\sigma d}\sum_{\vec{q}j}\frac{\partial N_0(\vec{q}j)}{\partial T}\sum_{\vec{k}l;\vec{k}'l'}\alpha(\vec{q}j;\vec{k}l,\vec{k}'l')[\vec{v}_{\vec{k}l}\tau_{\vec{k}l}\\-\vec{v}_{\vec{k}'l'}\tau_{\vec{k}'l'}]\cdot\vec{V}_{\vec{q}j}.\end{aligned} \tag{12}$$

Here σ is the electrical conductivity, d the dimensionality of the system, the two results from a sum over the spin degrees of freedom, $\vec{v}_{\vec{k}l}$ is the electron group velocity, and $\vec{V}_{\vec{q}j}$ is the phonon group velocity. The factor α is the relative probability that the $\vec{q}j$ phonon will scatter an electron from the state $\vec{k}l$ to the state $\vec{k}'l'$, relative to all other possible phonon collisions.

Details of the electron-phonon interaction are included in α. Symbolically

$$\alpha=\frac{\tau_{ep}^{-1}}{\sum\tau_{ep}^{-1}+\tau_p^{-1}}, \tag{13}$$

where τ_{ep} is the phonon relaxation time due to the electron-phonon interaction and τ_p is the phonon relaxation time due to any other interaction. This may include phonon-phonon, phonon-boundary, phonon-impurity, or phonon-defect scattering. Using the above results for the phonon relaxation rates Bailyn finds[22]

$$\alpha(\vec{q}j;\vec{k}l,\vec{k}'l')=\frac{I_{\vec{k}l,\vec{k}'l'}}{\frac{T}{\hbar\omega\tau_p(\vec{q})}\frac{\partial N_0}{\partial T}+\sum_{\vec{k}l,\vec{k}'l'}I_{\vec{k}l,\vec{k}'l'}}, \tag{14}$$

where

$$\begin{aligned}I_{\vec{k}l,\vec{k}'l'}=\frac{1}{2\hbar\omega k_BT}f_0[E(\vec{k}l)]\{1\\-f_0[E(\vec{k}'l')]\}N_0(\vec{q}j)\mathcal{M}(\vec{q}j)\delta(-)\delta_{\vec{k}',\vec{k}+\vec{q}}.\end{aligned} \tag{15}$$

Equations (12), (14), and (15) constitute Bailyn's theory of phonon drag in metals. The remainder of this article will be concerned with the application of this formalism to the case of metallic carbon nanotubes.

IV. BAILYN FORMALISM APPLIED TO METALLIC CARBON NANOTUBES

We consider a one-dimensional lattice lying on the z axis with left and right moving electrons with the band structure of a (10,10) armchair carbon nanotube. It is assumed that the electron relaxation time has a weak wave vector dependence for transitions about the K point ($2\pi/3a$ for lattice spacing a) so that $\tau(\vec{k}l+2\pi/3a)\sim\tau(2\pi/3a)$. Our expression for the phonon drag part of the thermopower then reads

$$\begin{aligned}S_{\text{drag}}=\frac{2|e|k_B\tau}{\sigma}\sum_{qj}\frac{\partial N_0(qj)}{\partial T}\\\times\sum_{\vec{k}l;\vec{k}'l'}\alpha(q,j;\vec{k}l,\vec{k}'l')[\vec{v}_{\vec{k}l}-\vec{v}_{\vec{k}'l'}]\cdot\vec{V}_{qj}.\end{aligned} \tag{16}$$

We note in passing that ignoring all but electron-phonon scattering reduces the drag to Eq. (1) when we take $\alpha=\delta_{\vec{k}',\vec{k}+\vec{q}}$.[18] The resulting sum over k,k' becomes $\hbar\omega$. We assert that this limit is not applicable to metallic carbon nanotubes.

To make progress we evaluate Eq. (16) using approximations valid for metallic carbon nanotubes. In these systems it is reasonable to assume that at small wave vectors and energies only acoustic phonons scatter electrons and that their dispersion is linear.[23] We then have

$$\vec{V}_{qj}=c_j\text{sgn}(q)\hat{z}, \tag{17}$$

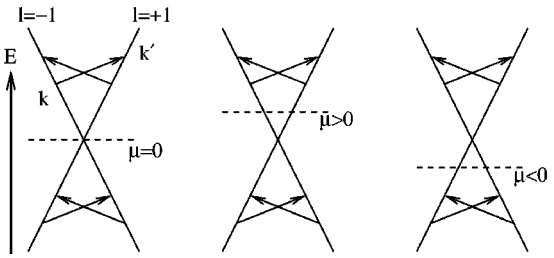

FIG. 1. The linear band model depicting energy along the y axis and wave vector along the x axis. The two bands shown, $l=+1$ and -1, cross at zero energy. The arrows indicate possible interband transitions from an initial electron state k to a final state k'. The dashed line indicates the position of the Fermi energy relative to the band crossing point, defined to be μ.

where c_j is the phonon speed in the jth band. The electronic band structure consists of two nearly linear bands crossing at zero energy, Fig. 1. This approximation holds as long as the Fermi level lies no more than ~ 1 eV from the band crossing. Above 1 eV other bands will complicate the spectrum. For carrier excitations around the K point we have

$$E(kl)=l\hbar v k, \tag{18}$$

where v is the Fermi speed and $l=+1,-1$ labels the two bands. With the linear band approximation the electron group velocity is then

$$\vec{v}_{kl}=\frac{1}{\hbar}\frac{\partial E(kl)}{\partial k}\hat{z}=vl\hat{z}. \tag{19}$$

Substituting the electron and phonon velocities into the expression for $S_{\rm drag}$ gives

$$S_{\rm drag}=\frac{2|e|k_B\tau v}{\sigma}\sum_{qj} c_j \mathrm{sgn}(q)\frac{\partial N_0(qj)}{\partial T} \times \sum_{kl;k'l'} \alpha(qj;kl,k'l')[l-l']. \tag{20}$$

Note that the above expression for the phonon drag vanishes when only intraband scattering is allowed, i.e., $l=l'$. In what follows we consider only interband scattering, $l\neq l'$. Define the transfer factor to be

$$t(q)\equiv \sum_{kl;k'l'} \alpha(qj;kl,k'l')[l-l'], \tag{21}$$

where α is given by Eqs. (14) and (15). The drag then has the simple form

$$S_{\rm drag}=\frac{2|e|k_B\tau v}{\sigma}\sum_{qj} c_j \mathrm{sgn}(q)\frac{\partial N_0(qj)}{\partial T}t(q). \tag{22}$$

To find $t(q)$ we need to evaluate the following expression:

$$\sum_{kl,k'l'} \alpha[l-l']=2\frac{\sum_{kk'} I_{k,1;k',-1}-\sum_{kk'} I_{k,-1;k',1}}{\frac{T}{\hbar\omega\tau_p(q)}\frac{\partial N_0}{\partial T}+\sum_{\vec{k}l,\vec{k}'l'} I_{\vec{k}l,\vec{k}'l'}}. \tag{23}$$

To simplify the expression for $t(q)$ we make an assumption regarding the available phonon scattering processes. Note that phonons traveling along a single nanotube may scatter through many different mechanisms. The large amount of surface area exposes the phonons to impurities, defects, and neighboring tubes. Furthermore, small tube lengths, $\sim 10\ \mu$m, allow for phonon-boundary scattering. We consider here two simple forms for the phonon relaxation time, valid at low and high temperatures, respectively. At low temperatures, the phonon decay mechanism is a competition between boundary and defect scattering which add no temperature dependence to the phonon relaxation time. At high temperatures, near room temperature, one expects phonon-phonon scattering to contribute significantly to phonon decay. Anharmonic scattering will require three phonons. The third being an optical mode at long wavelengths. The scattering rate will be proportional to the number of available optical phonons. One can then show that the relaxation time is inversely proportional to temperature, at large temperatures. We therefore take the following form for the phonon relaxation time

$$\tau_p=\tau_0\left(\frac{\phi}{T}\right)^m, \tag{24}$$

where ϕ is a characteristic temperature, $m=0$ for boundary/defect scattering, and $m=1$ for phonon-phonon scattering. Comparison with experiment will require a more accurate expression for τ_p.

We now invoke the assumption that mechanisms other than electron-phonon scattering limit the phonon lifetime, i.e., τ_p is small.[24] More precisely

$$\frac{T}{\hbar\omega\tau_p(q)}\frac{\partial N_0}{\partial T}\gg \sum_{kl,k'l'} I_{kl,k'l'}. \tag{25}$$

The above approximation enters phonon drag studies of quantum wires in GaAs. Analogous results for the phonon drag were also obtained in Ref. 25. The transfer factor becomes

$$t(q)\simeq \frac{2\hbar\omega\tau_p(q)}{T\frac{\partial N_0}{\partial T}}\times\left[\sum_{k,1;k',-1} I_{k,1;k',-1}-\sum_{k,-1;k',1} I_{k,-1;k',1}\right]. \tag{26}$$

To further evaluate the transfer factor we return to the matrix element in Eq. (15). Working with the deformable ion model at low wave vectors ($q\ll q_{\rm Debye}$) one finds[21]

$$\mathcal{M}(qj)=D_j(\hbar\omega_j)^2, \tag{27}$$

where D_j is a constant depending on the ion mass, the deformation energy, and other tube parameters including the radius and lattice spacing. This constant has been evaluated

for (10,10) carbon nanotubes.[26] The low wave vector approximation made above has been motivated by measurements of the Debye temperature. It has been measured to be near 1000 K in metallic carbon nanotubes.[17] It will be shown that, at low temperatures, the temperature dependence of the drag does not depend on the precise form of the matrix elements $\mathcal{M}$.

The transfer factor contains two terms of the form

$$\begin{aligned}\sum_{k,k'} I_{kl,k'l'} &= \frac{\mathcal{M}(qj)}{2k_BT\hbar\omega}\sum_{k,k'} f_0[E(kl)] \\ &\times\{1-f_0[E(k'l')]\}N_0(qj)\,\delta(-)\,\delta_{k',k+q} \\ &= \frac{\mathcal{M}(qj)}{2k_BT\hbar\omega}\sum_{k} f_0[E(kl)] \\ &\times\{1-f_0[E(k+q,l')]\}N_0(qj) \\ &\times\delta[E(k+q,l')-E(kl)-\hbar\omega], \end{aligned} \tag{28}$$

where the Fermi-Dirac distribution function is $f_0(E) = [e^{(E-\mu)/k_BT}+1]^{-1}$. The energy delta function in Eq. (28) needs to be evaluated for two cases. The first case is $l=1$ and $l'=-1$. We then have

$$E(k+q,-1)-E(k,1)-\hbar\omega=\hbar[-v(k+q)-vk-c|q|]=0. \tag{29}$$

This has a solution $k^a \equiv -(|q|/2)\mathrm{sgn}(q)+c/v$. The second case is $l=-1$ and $l'=1$. The solution for this case is $k^b \equiv -(|q|/2)\mathrm{sgn}(q)-c/v$. Upon a change of variables in the energy delta function of Eq. (28) the sum can be evaluated. The transfer factor now becomes

$$\begin{aligned} t(q) = \frac{\tau_p(q)}{\dfrac{\partial N_0}{\partial T}}\left(\frac{\mathcal{M}(qj)}{k_BT^2}\right)\left(\frac{N_0(qj)L}{4\pi\hbar v}\right)\times[f_0(\hbar v k^a)\{1 \\ -f_0(\hbar v k^b)\}-f_0(-\hbar v k^b)\{1-f_0(-\hbar v k^a)\}], \end{aligned} \tag{30}$$

where L is the tube length. Substituting the transfer factor into our expression for the drag, Eq. (22), gives

$$\begin{aligned} S_{\mathrm{drag}} = \frac{|e|\tau v}{\sigma T^2}\,\frac{L}{2\pi k_B\hbar v}\sum_{qj} c_j\,\mathrm{sgn}(q)\,\mathcal{M}(qj)\,\tau_p(q)N_0(qj) \\ \times[f_0(\hbar v k^a)\{1-f_0(\hbar v k^b)\} \\ -f_0(-\hbar v k^b)\{1-f_0(-\hbar v k^a)\}]. \end{aligned} \tag{31}$$

To evaluate the sum over j it is convenient to assume that only one linear phonon branch contributes to the thermopower. The inclusion of other linear modes with approximately the same phonon speed will simply add to the overall constant. Passing to the continuum limit and imposing a Debye cutoff q_D one can show that

$$\begin{aligned} S_{\mathrm{drag}} = \frac{|e|\tau cL^2}{2\pi^2\sigma T^2 k_B\hbar}\int_0^{q_D} dq\,\mathcal{M}(q)\,\tau_p(q)N_0(q)\times[f_0(\hbar v k^a)\{1 \\ -f_0(\hbar v k^b)\}-f_0(-\hbar v k^b)\{1-f_0(-\hbar v k^a)\}]. \end{aligned} \tag{32}$$

To further simplify the drag formula we make a change of variables with the following definitions:

$$\begin{aligned} u &\equiv \frac{\hbar cq}{2k_BT}\left(\frac{v}{c}-1\right), \\ \overline{f}(x) &\equiv \frac{1}{e^{(x-\mu/k_BT)}-1}, \\ \gamma &\equiv \frac{v+c}{v-c}. \end{aligned} \tag{33}$$

The drag can then be written as

$$\begin{aligned} S_{\mathrm{drag}} \simeq \frac{|e|\tau cL^2}{\pi^2\sigma\hbar^2 Tv}\int_0^{T_Dv/2cT} du\,\frac{\mathcal{M}\tau_p}{e^{2uc/v}-1} \\ \times[\overline{f}(-u\gamma)\{1-\overline{f}(-u)\}-\overline{f}(u)\{1-\overline{f}(u\gamma)\}], \end{aligned} \tag{34}$$

where the Debye temperature is defined as usual $T_D \equiv \hbar cq_D/k_B$. In the above we have used the fact that for (10,10) arm chair carbon nanotubes $c=20.35\times10^3$ m/s[23] for the longitudinal acoustic mode whereas $v=8.4\times10^5$ m/s. This gives $v/c\sim100$. Equation (34) is our primary result and contains several interesting features. First note that when $\mu=0$ we have $\overline{f}(-x)=1-\overline{f}(x)$, in which case the two terms in the integral cancel giving no contribution to the thermopower. If we take $\mu>0$ then the second term dominates, giving a negative contribution to the thermopower. Similarly, if we take $\mu<0$ we get a positive contribution to the thermopower.

The overall sign of S_{drag} can be deduced from Fig. 1. For $\mu>0$, interband transitions above the crossing point are favored. Transitions with $q>0$ yield a positive change in the electron group velocity which, from Eq. (16), give an overall negative sign to the drag. For $\mu<0$, interband transitions below the crossing point are favored which give and overall positive sign to the drag.

The Debye temperature plays a small role because the kernel of the integral is sharply peaked. As long as the peak $u_{\mathrm{pk}}=\mu/k_BT$ lies within the range of integration the Debye temperature can be set to infinity. When the peak crosses the range of integration, $\mu\sim k_BT_Dv/2c$, S_{drag} falls to zero. For, $\mu>k_BT_Dv/2c$ the set of transitions favored by the electron distribution require wave vectors above the Debye cutoff q_D.

Figure 2 shows the temperature dependence of S_{drag}. To evaluate the integral we have taken the deformable ion model, Eq. (27). We have also taken a temperature independent phonon relaxation time, $m=0$ in Eq. (24). For large temperatures S_{drag} flattens because we assume here that τ_p does not depend on temperature. In real samples it is likely

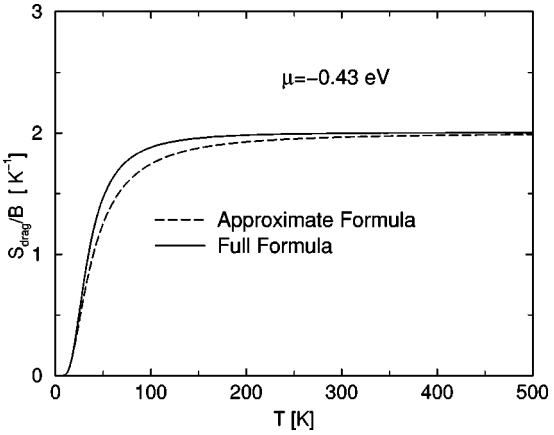

FIG. 2. The phonon drag contribution to the thermopower plotted, in units of the constant B, as a function of temperature. The Fermi energy is chosen to be $\mu=-0.43$ eV. The ratio between the electron and phonon speeds is taken to be $v/c=100$. The solid line shows the result from the full formula, Eq. (34) with $T_D=1000$ K. The dashed line shows the simplified approximation, the second term in Eq. (2). For purposes of comparison, a temperature independent phonon relaxation time is assumed, $m=0$ in Eq. (24).

that, for large temperatures, phonon-phonon scattering may impose a temperature dependence to the phonon relaxation time. We would then see a change in the drag at large temperatures. In Fig. 3 we compare the temperature dependence of the drag for the two cases $m=0$ and $m=1$ in Eq. (24). Here we have taken $\phi=100$ K, $v/c=100$, $\mu=0.436$ eV, and $T_D=1000$ K. A suppression of the drag at large temperatures clearly induces a peak, similar to those observed in experiments. The low temperature behavior can be extracted with a few approximations.

V. THE LOW-TEMPERATURE LIMIT

A low-temperature approximation to the integral formula for $S_{\rm drag}$, Eq. (34), can be obtained for nonzero values of μ.

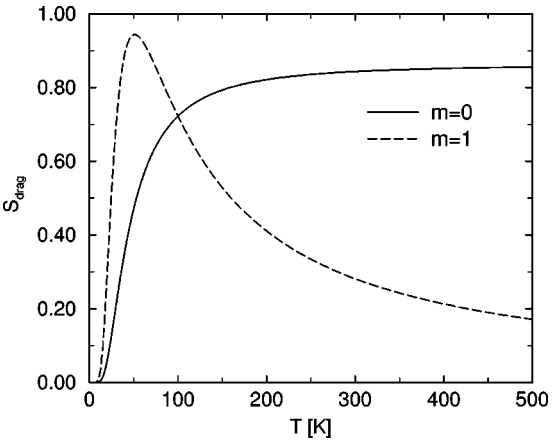

FIG. 3. The phonon drag contribution to the thermopower plotted versus temperature for two different cases. The solid line shows the drag when a temperature independent phonon scattering mechanism dominates phonon decay, $m=0$ in Eq. (24). The dashed line shows the drag when phonon-phonon scattering dominates, $m=1$. The Fermi level is chosen to be $\mu=-0.5$ eV. The parameter B is the same for both curves. We also take $v/c=100$ and $\phi=100$ K.

For $\mu<0$ the second term in the integrand vanishes. We then have

$$S_{\rm drag}\simeq\frac{|e|\tau cL^2}{\pi^2\sigma\hbar^2Tv}\int_0^{T_Dv/2cT}du\,\frac{\mathcal{M}\tau_p}{e^{2uc/v}-1}\times[\overline{f}(-u\gamma)\{1-\overline{f}(-u)\}]. \tag{35}$$

As mentioned earlier the factor $\overline{f}(1-\overline{f})$ in the integral is a sharply peaked function centered at the value $u_{\rm pk}\approx\mu/k_BT$. Thus

$$S_{\rm drag}\simeq\frac{|e|\tau cL^2}{\pi^2\sigma\hbar^2Tv}\,\frac{\mathcal{M}(2\mu/\hbar v)\tau_p(2\mu/\hbar v)}{e^{2u_{\rm pk}c/v}-1}\times\int_0^{T_Dv/2cT}du[\overline{f}(u)\{1-\overline{f}(u\gamma)\}]. \tag{36}$$

The integral can now be performed giving

$$\int_0^{T_Dv/2cT}du[\overline{f}(u)\{1-\overline{f}(u\gamma)\}]=1+\frac{\mu c}{vk_BT}+\vartheta(\{\gamma-1\}^2). \tag{37}$$

The above argument remains the same for the case $\mu>0$ except for an overall sign change. The low-temperature drag contribution to the thermopower becomes the second term in Eq. (2), where the temperature independent factor $B\equiv(|e|\tau cL^2/\pi^2\sigma\hbar^2v)\mathcal{M}(2\mu/\hbar v)\tau_0(2\mu/\hbar v)\phi^m$ may be taken as a fitting parameter. Note that the low-temperature limit is easily reached because $v/c\gg1$. Figure 2 compares the above approximation to the full formula given by Eq. (34).

Fermi statistics restricts the interband transitions to lie near the Fermi level, thereby excluding all but a narrow range of phonon wave vectors. Eq. (2) therefore applies to systems with any, nonsingular q dependence in the electron-phonon matrix elements. Only the constant B will change with different forms of electron-phonon coupling.

Fitting Eq. (2) to measurements of $S_{\rm total}$ versus temperature yields a rough estimate of μ. Figure 4 shows the total thermopower for three possible values of μ. Motivated by experiments on mats of single-walled carbon nanotubes[3] we assume that the parameter A changes sign with the Fermi level. We have kept the ratio $|A/B|$ fixed. In experiments we expect the parameters A and B to have a nontrivial dependence on μ due to sample dependent variations in the phonon and electronic density of states.

VI. CONCLUSION

We have shown that within a one dimensional model phonon drag resulting from interband transitions between two linear bands gives a nonlinear temperature dependence to the thermopower when the Fermi level does not lie at the band crossing. Assuming that mechanisms other than the electron-phonon interaction contribute to phonon scattering we derive a simple expression for the phonon drag contribution to the thermoelectric power in a model that approximates parameters found in single walled (10,10) carbon nanotubes. The

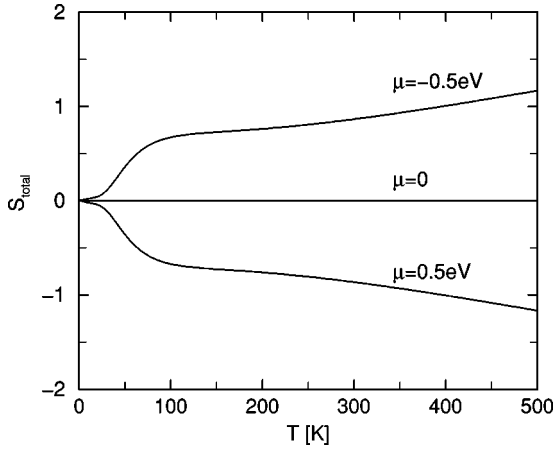

FIG. 4. The total thermopower, Eq. (2), plotted versus temperature for two values of the Fermi level, $\mu=-0.5$ and 0.5 eV. The ratio of the two-fitting parameters is taken to be $|A/B|=10^5$. The top curve has a positive value for A while the bottom curve has a negative value for A. We also have $v/c=50$, $\phi=100$ K, and $m=1$. The central line is the $\mu=0$ case in Eq. (34), where $A=0$. For $\mu=0$ transitions above and below the Fermi level cancel to give no net thermopower.

strength of the effect depends strongly on the position of the Fermi level.

The above results suggest that the phonon drag effect is a good candidate for recent, low-temperature anomalies in thermopower measurements on single-walled carbon nanotubes. We note, however, that, as is typical in theories of the phonon drag effect in conventional metals, the size of the fitting parameter B is difficult to estimate from first principles.

In applying the above formalism to low-temperature peaks in thermopower measurements under different ambient conditions it is important to account for different scattering mechanisms. Different scattering mechanisms in nanotubes can exhibit drastically different behavior, in analogy to the wide variety of phonon drag effects seen in conventional metals with different alloys. In this work we have assumed that the electron relaxation time τ is independent of temperature and that τ_p goes as $1/T^m$. From Fig. 4 we see that phonon-phonon scattering induces a peak in S_{total}. The $m=1$ case therefore appears be a good approximation for the samples of Ref. 3. Figure 3 also demonstrates that a temperature independent scattering mechanism $(m=0)$ produces only a knee in S_{total}. Weak inflections in the thermopower have also been observed in many thermopower measurements on carbon nanotubes. Other conditions may favor a decay mechanism which can significantly alter the temperature dependence of the drag thermopower. Detailed comparison with experiment will require suitable choices for the temperature dependence of the phonon lifetime.

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